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CANADIAN PATENT

⑤④ HEAT RESISTANT ALLOY FOR CARBURIZATION
RESISTANCE

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ABSTRACT OF THE DISCLOSURE

Catastrophic carburization of metal furnace tubes which take place when heating hydrocarbons is minimized by using an alloy which when oxidized forms a protective manganese and chromium oxide scale. In practice this is done by contacting the hydrocarbons with a heated metal surface that has an adherent layer of manganese and chromium oxide on the metal surface which is in contact with the hydrocarbon. The protective scale of manganese and chromium oxide is formed on the surface of an alloy consisting essentially of chromium, iron and nickel as well as manganese, by adjusting the nickel content of the alloy to the range of 36 to 38% and the manganese content of the alloy from 1.25 to 2.0%, forming the alloy into a metal surface, and thereafter, treating the metal surface with steam at elevated temperatures for a time sufficient to oxidize manganese and chromium present in the alloy and form a protective scale of manganese and chromium oxide.

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1 This invention relates to a technique for
2 minimizing carburization of furnace tubes exposed to
3 hydrocarbons under pyrolysis and reforming conditions.

4 In processes for the controlled pyrolytic de-
5 composition of hydrocarbons, typically, the hydrocarbon
6 is decomposed at high temperatures under varying pressure
7 conditions in the presence of predetermined amounts of
8 steam.

9 It has been well recognized that the above-
10 mentioned cracking and reforming processes when conduct-
11 ed in the presence of certain metals and metal alloys
12 often lead to excessive deposition of carbon. These
13 carbon deposits reduce the size of the furnace tubes
14 with concomitant problems of plugging, and also affect
15 the strength of the metal furnace tubes resulting in
16 structural failure of the metal tubes. In such in-
17 stances such failure is frequently referred to as catas-
18 trophic carburization of the metal.

19 It is known for example that iron surfaces
20 will have a catalytic effect upon the pyrolysis of
21 hydrocarbons, promoting carbon formation. The carbon
22 formed is absorbed or diffused into the metal resulting
23 in the structural failure of the metal. Consequently,
24 numerous techniques have been proposed for avoiding such
25 catastrophic carburization of metal tubes by alloying
26 the iron and/or by forming protective coatings of an
27 oxide on the surface of the metal to be contacted with
28 the hydrocarbon under the reforming or pyrolysis condi-
29 tions. None of these techniques have provided a complete
30 panacea and there still is a commercial interest in

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1 preventing carburization of furnace tubes.

2 According to the present invention, there is
3 provided a method of heating hydrocarbon carbons in con-
4 tact with metal surfaces under conditions which normally
5 would cause difficulties due to carburization of the metal
6 surfaces which comprises contacting the hydrocarbons of
7 the metal surface containing adherent oxide layer of
8 manganese and chromium, whereby heat is passed from the
9 metal surface to the hydrocarbon without significant
10 carburization of the metal.

11 Thus, in one aspect the present invention
12 contemplates a method of rendering metal surfaces ex-
13 posed to hydrocarbons under pyrolysis and reforming con-
14 ditions resistant to carburization by providing on such
15 metal surfaces in contact with the hydrocarbons an ad-
16 herent layer of manganese and chromium oxide.

17 In yet another aspect of the present invention,
81 an adherent layer of manganese and chromium oxide is
19 formed on a metal alloy surface by oxidizing a nickel-
20 chromium-iron alloy that has at least 36% nickel and
21 from 1.25% to 2.0% manganese.

22 The present invention can be carried out for
23 example by passing a hydrocarbon through a heating means
24 having one or more tubes or conduits which are heated
25 directly or indirectly to transfer heat to the hydro-
26 carbon. The metal surfaces to be used in accordance
27 with this invention should have an adherent coating
28 of manganese and chromium oxide.

29 In a particularly preferred embodiment of the
30 present invention the metal tubes are formed from an

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1 alloy consisting essentially of chromium, nickel and
2 iron and having at least 1.25% manganese and at least
3 36% nickel. For example, the alloy may have from 36
4 to 38% nickel, from 23 to 27% chromium, and from 1.25%
5 to 2% manganese. Indeed such an alloy when contacted
6 with steam at elevated temperatures for a time suf-
7 ficient to oxidize some of the manganese present in the
8 alloy results in the formation of an adherent protective
9 coating of manganese and chromium oxide which is resis-
10 tant to carburization. For example, the metal surfaces
11 are pretreated with steam at temperatures in the range
12 of 500°F. to about 2000°F., and preferably at about
13 1500°F. for from about 24 hours to about 96 hours, such
14 as about 72 hours.

15 Equally important in providing an adequate
16 protective coating of manganese and chromium oxide on
17 the surface of the metal is the grain structure of the
18 contact surface. It has been discovered that with fur-
19 nace tubes, for example, the interior contact surface
20 should be made up of equiaxed grain structure. Basic-
21 ly the grain structure is achieved by casting the
22 alloy into a tube and controlling the thermal gradient
23 during solidification. Any other technique known in
24 the art for controlling grain structure can be employed.

25 The invention will be better understood by
26 reference to the following examples and demonstrations.

27 EXAMPLE 1

28 A series of tubes having a 4-inch inside
29 diameter were installed in a furnace and were pretreated
30 with steam at 1450°F. for 72 hours.

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Hydrocarbons were fed through the tubes in contact with the interior surfaces of the metal. The metal tubes were maintained at temperatures generally of the order of 1900°F. In these tests, two alloy compositions were used. The alloy compositions are set forth in Table I below.

TABLE I

	<u>Alloy 1</u>	<u>Alloy 2</u>
Carbon, %	0.4-0.5	0.43
Manganese, %	1.09	1.30
Silicon, %	1.01	1.10
Chromium, %	28.0	23.5
Nickel, %	19.0	37.0
Molybdenum, %	0	1.89
Iron, %	Balance	Balance

At the end of 30,000 hours on stream the furnace tubes were physically inspected. Those tubes of alloy 1 were, at least in some instances, carburized as much as 80% and had as little as 2/3 of an effective wall thickness remaining. Those of alloy 2 were effectively protected against carburization. Magnetic readings of the tubes of both alloy 1 and alloy 2 showed that the protected regions were predominantly oxides of manganese and chromium whereas the unprotected areas were predominantly oxides of iron.

In a more detailed analysis performed with a microprobe analyzer, it was surprisingly discovered that a continuous layer of manganese oxide was lying outside the chromium oxide layer and close to the surface and the highly protected layers. Indeed, in

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1 alloy 2 the thickness of the manganese oxide scale was
2 about 10 times greater than the amount of manganese
3 oxide scale in alloy 1.

4 Apparently, a nickel content, in a nickel-
5 chromium-iron alloy, of greater than 36% and a mangan-
6 ese content of greater than 1.25% is necessary to pro-
7 vide a good protective scale of manganese and chromium
8 oxide in the interior surface of the furnace tube.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for heating hydrocarbons by contact with heated metal surfaces containing nickel and iron under conditions which are likely to result in carburization of the metal, characterized by contacting said hydrocarbons with a heated metal surface that has an adherent layer of manganese and chromium oxide on the metal surface which is in contact with the hydrocarbon, whereby the metal is protected against carburization and heat is passed from the metal to the hydrocarbon.
2. The method of claim 1 wherein said hydrocarbon is contacted with said metal surface at an initial temperature in the range of about 1700°F to 2000°F.
3. The method of claim 1 wherein the metallic surface comprises the inner walls of heat exchanger tubes suitable for heating said hydrocarbon.
4. A method of forming a protective scale of manganese and chromium oxide on the surface of alloy consisting essentially of chromium, iron and nickel as well as manganese characterized by:
 - (1) adjusting the nickel content of the alloy to the range of 36 to 38% and the manganese content of the alloy from 1.25 to 2.0%;
 - (2) forming the alloy into a metal surface; and
 - (3) thereafter, treating the metal surface with steam at elevated temperatures for a time sufficient to oxidize manganese and chromium present in the alloy and form a protective scale of manganese and chromium oxide.

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5. The method of claim 4 wherein the metal is treated with steam at temperatures in the range of 500°F to 2000°F for at least about 24 hours.

6. The method of claim 4 wherein the metal is treated with steam at a temperature of about 1450°F for about 72 hours.